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The use of strip-to-wire mill to make metal powder-filled cored wires has demonstrated an effective methodology for making specialty welding consumable wires for the U.S. Army where their use is of low volume but essential to the manufacture or maintenance of special technical assemblies. Special attention has been given to the welding of light metals (Aluminum and magnesium alloys). Aluminum welding metallurgy and practices were reviewed and described in a chapter for the Handbook of Aluminum Metallurgy, Process and Equipment. The weldability of magnesium alloys was investigated because new magnesium alloys are being developed to reduce weight in vehicles. To evaluate the service life of time-dependent alloys (i.e. Superalloys relative to TCP intermetallic phase and aluminum precipitation strengthened alloys) and to determine the acceptability of a weld repair relative to its service life (fatigue), new nondestructive techniques are being developed based on electronic and magnetic property measurements.

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ABSTRACT

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1.0 INTRODUCTION

The development of new methodologies for highly-portable field repair welding has been performed. Field welding repair is essential to maintain the effective use of machinery, mobile structures (light portable bridges and light watercraft) and technical assemblies (trucks, armor vehicles, etc.). Today, this requirement must address the advances in high strength low alloy steels, new aluminum and other light materials. The primary hindrance in having field weld repair systems, as advanced and as flexible as today's Army, are the following:

1. The weight and bulkiness of the present welding power sources, and wire feeding and control systems are a liability to the needed mobility.
2. The Army is on the forefront in using advanced structural materials, such as advanced higher strength steels, titanium, and aluminum, in portable structures and vehicles to achieve air mobility. The weldability, especially for field repair, requires special welding consumables.
3. Present welding practices require developed skills in addition to the numerous functions that Army personal must perform. It is very desirable to have welding processes that are more amenable to a wide range of personal skills. This "welder friendly" system is achievable through innovations in both power source controls and welding consumables.
4. Shielding gases for welding are a special burden to a mobile force. It requires repair personnel to use specific flux assisted welding processes and/or provide and handle bottled shielding gases. New self-shielded welding consumables and practices need to be developed to support mobility and to cope with various field environments.

This investigation addressed both the development of field repair welding consumables and included the manufacturing of specialty welding consumables for defense applications where there is insufficient demand to guarantee and maintain the supply of needed welding consumables.

With aluminum structural and machinery components offering major weight reduction for a mobile army, the ability to field repair is an important requirement. In general, aluminum welding requires more training and has specific metallurgical difficulties, especially for the higher strength aluminum alloys. The field repair requirement increases the need for new approaches for aluminum welding consumables. CSM has been investigating grain refinement in the aluminum weld deposit. Weld grain refinement reduces the susceptibility to hot cracking and assists in maintaining the mechanical properties. CSM has been developing a metal-filled cored aluminum wire so that the grain refiner can be introduced into the weld deposit as grain refining inoculants. This effort has investigated the potential use of intermetallic inoculants.

The weldability of other light metals, such as magnesium has, also been investigated. Electronic and magnetic property measurements to determine the susceptibility were used to form specific intermetallic phase and to quantify specific microstructural constituents in high alloys. The project has been developing a PHACOMP meter to determine nondestructively, the tendency to form Topological Close Packed phase in high alloys. This project is utilizing the advanced analytical instruments placed at CSM by the DURIP instrument grant program.

The following sections have more comprehensive descriptions of the achievements of this ARO sponsored welding consumable research.

2.0 ACCOMPLISHMENTS

2.1 Development of Exothermically Assisted and Self-Shielded Flux Cored Arc Welding Consumables

Presently, field repair welding requires bulky dedicated electrical equipment and/or gas bottles with attendant torches, hoses, and regulators, as well as considerable operator skill. The electrical dependency can at least be minimized and the gas requirements eliminated with the proper incorporation of chemical heating reactions within the flux of traditional flux containing arc welding processes. A side benefit of a minimal arc dependency is a concomitant reduction in operator skill level and a widening of the range in acceptable welding parameters. Portability and applicability can be enhanced with the concentration of chemical heat at the point of welding and the reduction or near elimination of the welding process on electrical power dependence.

ARO sponsored research at the Colorado School of Mines (1) has shown that exothermic additions (utilizing traditional reactions) into the flux of electrodes in the SMA welding process definitely increases the heat input into the weld for a given amount of electrical power. The heat input, measured with a liquid nitrogen calorimeter, was shown for SMA welding to go through a peak with increases in exothermic constituent flux concentration levels. The rise and then falling off of the observed heat input with increasing exothermic powder concentration in the flux system is shown in Figure 1. A practical maximum was found with a mixture of the aluminum thermite rather than with the more potent (heat wise) magnesium thermite. Apparently a major limitation to the amount of exothermic flux addition in the effective utilization of this heat for welding is the lack of heat constriction at the arc-electrode interfacial area. Also, the ample availability of atmospheric oxygen along the outside of the covered electrode apparently allows the thermite reaction to advance up the rod and away from the arc. The exothermic addition greatly assists the deposition efficiency of the electrode (from an electrical power consumption perspective), but does little to promote penetration. The Lorentz force promotes weld pool penetration at higher currents and is actually more efficient in achieving deeper welds than the external chemical reactions. After a point, further chemical heat additions to the flux serve only to burn back on the electrode during welding.

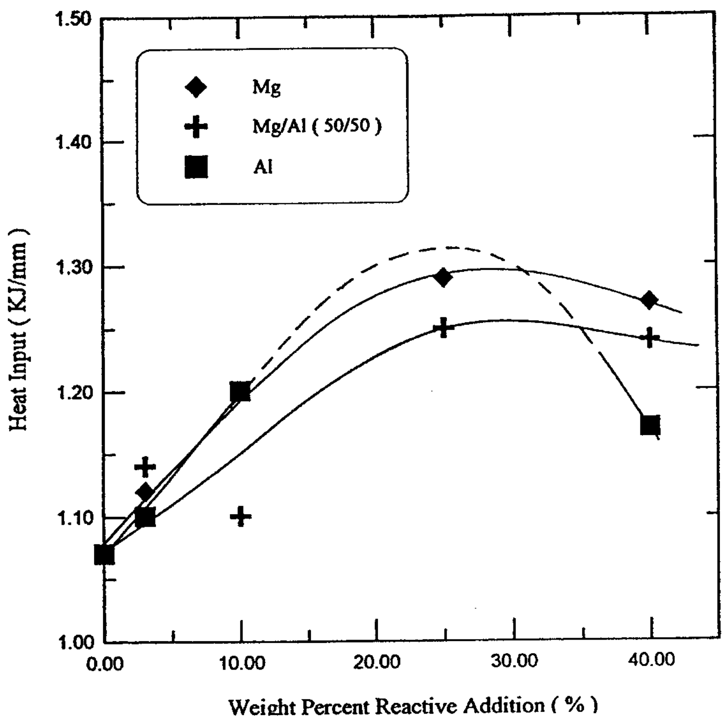

Figure 1. – SMA welding plot of measured heat input as a function of weight percent addition (1).

The effectiveness (in terms of heating potential) of exothermic chemical additions to the flux in the Flux-Cored Arc (FCA) welding process was also investigated. It was the logical follow-on task of a prior ARO sponsored work (1) in which the heating potential of exothermic additions were characterized in the Shielded Metal Arc (SMA) welding process. The reaction of traditional Thermit* mixtures, aluminum powder plus hematite, and magnesium powder plus hematite, are known to produce enough heat energy to weld (2). If the types and amounts of chemical reactions can be controlled such that exothermic reactions predominate, then this chemical heat can supplant much of the heat of a conventional arc, theoretically to the point of eliminating the need for the electric arc itself.

In the case of both the prior SMA welding work and this FCA welding work, a baseline flux formula was modified with mixtures of the traditional exothermic additions. Aluminum plus hematite, magnesium plus hematite, and a fifty-fifty mix of the aluminum and magnesium types of exothermic reactions were prepared and evaluated.

A strip-to-tube cored wire-forming bench was acquired, modified, and put into service at CSM. The

A strip-to-tube cored wire-forming bench was acquired, modified, and put into service at CSM. The strip is pulled from a vertical payout wheel, travels through the adjustable forming wheels into a trough just below the flux hopper where the flux load is channeled into the open "u" of the strip, and then through the final three closure wheels. From the closure wheels the tube is pulled through two or three reducing dies in a die box and then spooled onto the bull wheel. Several more die reduction passes through the die box are necessary before the wire is cleaned and spooled onto a reel compatible with the welding machine.

Wires with exothermic additions were welded under controlled processing parameters. Welding parameters were systematically changed to allow proper analysis of processing effects. The resulting welds were calorimetrically measured to determine the heat input as a function of exothermic addition content to the cored wire.

By physically containing the flux and hence flux reactions within a central core of the wire electrode in the FCA welding process, the limitations encountered in the SMA welding research were partially avoided. During the SMA, welding increase the exothermic additions beyond a critical limit causes accelerated burning along the covering and away from the melting tip of the electrode. No premature or otherwise uncontrolled exothermic reactions were observed with FCA welding consumable. By limiting the available oxygen to that supplied only by the flux constituents, the thermite reaction rate can be tailored precisely to that of the melting rate of the metal sheath and more localize the reaction to the electrode tip area. Thus, the resulting chemical heat generation is more physically constricted to the immediate arc region.

A peak in measured heat input with percent magnesium type flux addition, similar to the peak found in the SMA welding case (see Figure 2), was observed. A peak in the measured heat input is indicative of the function passing through an optimal efficiency condition. As the percentage of magnesium plus hematite in the flux increased, the arc was observed to get subjectively brighter. Obviously, the magnesium was burning in the arc. These results suggest an increase in the electrode extension (stick out) to focus the heat transfer to the weld pool. Figure 2 shows the measured heats as a function of percent magnesium type exothermic flux concentration for melting rates of from 200 to 300 ipm (508 to 762 cm per minute) in steps of 25 ipm (63.5 cm per minute).

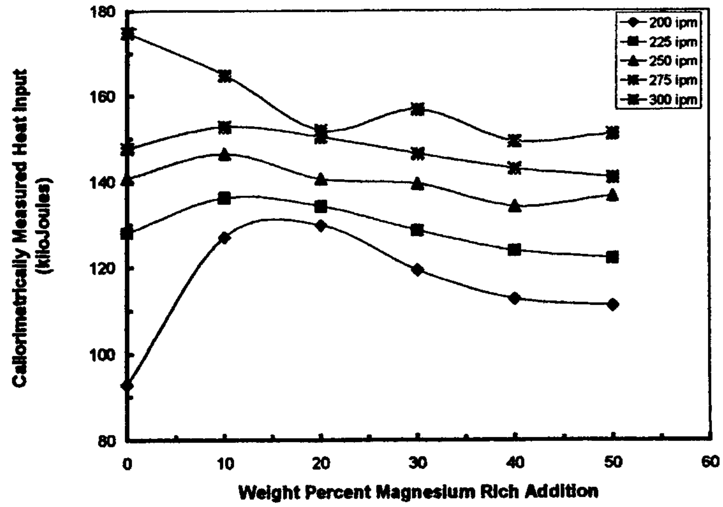

Figure 2. – Measured heat input as a function of weight percent addition for magnesium rich type flux at 200 to 300 inches per minute melting rate.

Figure 3 reveals the unexpected eight percent rise in measured heat input opposite the eight percent reduction in electrical power consumed in the area of ten and twenty weight percent additions. The excess heat can only be explained by the generation of chemical heat. The other anomaly is the linear decrease in both the measured heat input and the electrical power consumed at thirty weight percent and beyond. The slope in the reduction of measured heat input is less than the slope for the electrical power decrease. The likely indication is that chemical heating in the higher concentration levels is still significant.

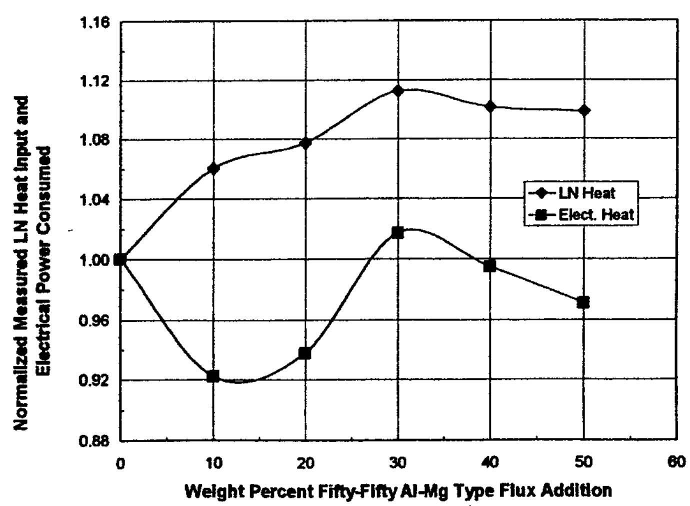

Figure 3.– Normalized measured LN heat input and electrical power consumed as a function of weight percent aluminum type flux addition at 110 ipm melting rate.

2.1.1 Summary of Results: Exothermic Assisted Consumable Development

Exothermic additions to the flux of the FCA welding consumable electrode has resulted in measurable increases in the melting efficiency. Acceptable weld bead morphologies were produced with no external shielding at reduced electrical power consumption. The presence of iron powder is beneficial in moderating the exothermic flux reactions. The prior SMA investigation saw maximum gain with small amounts of the aluminum type addition while this investigation with the FCA process found maximum gains with the fifty-fifty A1-Mg type additions. The exothermic reactions are quite contained with the FCA process. Perhaps a combination of the two processes could result in an exothermic addition filled cored SMA rod electrode whereas the external flux coating could be configured for the traditional role of arc stability and weld bead protection.

Field repair welding can be enhanced through the use of exothermic flux additions to the FCA welding process. The self-shielding nature of the process precludes the need for gas systems and the desensitization of the welding parameter space broadens the user appeal and applicability. The measured reduction in electrical energy consumed brings the process into the realm of possibility for use with a common twelve volt battery.

2.2 Development of Aluminum Weld Repair Welding Consumables

The use of aluminum alloys has been limited due to their weldability and the weldability difficulties are enhanced with the conditions common to field weld repair. Aluminum alloys are susceptible to a high occurrence of weld cracking defects. These defects have a significant effect on the strength and integrity of the welded aluminum structures. By controlling the grain size during the solidification of the weld metal, weld defects can be minimized or eliminated. Therefore grain size has been of great interest in the welding of aluminum alloys.

Grain refinement improves the strength and toughness of welds by providing an equiaxed rather than a columnar grain structure (3). Grain refinement increases the grain boundary surface area and reduces the concentration of contaminates which segregate to the grain boundaries. The influence of grain size on the strength can be expressed by the Hall-Petch equation, which relates the yield strength to grain size at constant strain values (4-6). Several different researchers have studied many different alloy systems in an attempt to identify the nucleation mechanism in aluminum alloy systems. Many different transition metals

additions have been added to aluminum alloys to control the grain size. These studies have identified different intermetallics as nucleants and grain refiners in aluminum alloys as shown in Table I (7-26). The following intermetallics are known as nucleants for aluminum alloys: $ScAl_3$, VAl_{10}, $ZrAl_3$, AlB_2, $TiAl_3$, CrA_{17}, and $NiAl_3$. Many of the intermetallics shown in Table I are the first intermetallic formed on the aluminum rich side of the binary phase diagram.

Table I: Known Intermetallic Nucleants and Their Strukturbericht Designations for Aluminum Alloy Systems

Reported Nucleants for Aluminum Alloys	Strukturbericht Designation	Pearson Symbol	Space Group
$ScAl_3$	L12	cP4	Pm3m
VAl_{10}	CF_{184}	cF_{176}	Fd3m
$ZrAl_3$	DO_{23}	cP4	Pm3m
AlB_2	C_{32}	hP3	P6/mmm
$CrAl_7$	C_{34}	mC 104	C2/m
$NiAl_3$	DO_{20}	cP4	Pm3m
Ti_3Al	DO_{19}	hP8	P63/mmc
TiAl	Ll_0	tP4	P4/mmm
$TiAl_3$	DO_{22}	tI8	I4/mmm

Previous research (12) has shown that titanium aluminide (Al_3Ti) and zirconium aluminide (Al_3Zr) particles provide nucleation of new grains and grain refinement in aluminum welds and cast alloys. The Al_3Ti and Al_3Zr phases have been shown by research at the Colorado School of Mines to be susceptible to dissolution during multiple welding passes. This dissolution can eliminate their effectiveness as grain refining agents for second or subsequent passes on multi-bead welds. Kerr, et. al. (23) noted that at high cooling rates it is possible to suppress the formation of the intermetallic phase in the aluminum-titanium alloy system. This effect is probably caused by the inability of the intermetallic phase to form in the weld pool during the welding cycle and means that the intermetallic phase particles must be present in the welding consumable prior to welding. The presence of titanium or zirconium as a weld metal constituent is not a sufficient condition for grain refinement of the weld deposit. The elemental additions must be present as an intermetallic phase in the welding consumable. The dissolution and difficult precipitation of the nucleating intermetallic particles emphasize the importance of the influence of weld pool solidification kinetics on the grain refining response achieved by the addition of nucleating agents.

Many investigators have reported on their experiences concerning the dissolution times for the

$TiAl_3$ intermetallic crystals in molten aluminum. Dissolution times have ranged from less than 30 seconds (24), to several minutes (25), and in some cases a period of several hours (26). Thus, for the case of a weld pool environment where the intermetallic size and distribution will be much finer owing to the welding consumable processing route, a theoretical analysis was performed to represent the particle size range and dissolution environment found in the weld pool environment. The analysis is similar to one presented by Araberg, Backcrud and Klang, adjusted for the particle size and thermal conditions observed in the experimental welds. The theoretical dissolution times were calculated for an intermetallic particle size range that was experimentally observed to occur in the alloy insert strips used to make the titanium and zirconium additions. The calculated dissolution times show that for a temperature of 700 °C particles of a size equal to or less than a micron will dissolve in a matter of a few seconds. The dissolution rate is even greater at a temperature of 800 °C at which particles equal to or less than about 5.0 microns are dissolved in a few seconds. The significance of this theoretical result becomes apparent when an estimate is made of the time a particle spends in the weld pool. A simple way of finding the minimal time a particle spends in the weld pool is to assume it remains stationary as the weld pool moves past. The residence time is calculated by dividing the length of the weld pool measured at the centerline by the travel speed.

The analysis of these residence times shows the minimal weld pool exposure times for an intermetallic particle to be on the order of one to several seconds. These results are significant because the residence times are of the same magnitude as the calculated dissolution times for the particles contained in the welding consumable. The retention of smaller particles by limiting the exposure time increases the number of heterogeneous nucleation events and assists in grain refinement.

Recently, it was found that scandium additions are extremely effective in refining the grain size of aluminum castings and weldments (27, 28). Ishchenko and Labur postulated that scandium tri-aluminide ($ScAl_3$) provided an excellent surface (coherency) for nucleation and growth because it is coherent with aluminum and has a similar lattice parameter. Unfortunately, scandium is too expensive and its foreign source too sensitive to be considered for most applications.

Mousavi investigated the effect of additions with high temperature eutectics on the grain refinement of aluminum welds. He found that of the four elements investigated, the grain refinement effectiveness could be ranked from best to worst: scandium, iron, manganese, and cobalt. Also, circular patch welds were done to confirm the effectiveness of the grain refinement to reduce hot cracking in an alloy 7108 with scandium and Tibor™(contains $TiAl_3$, AlB_2, $(Ti, Al)B_2$, and TiB_2) additions. Tibor is already known to be an

effective grain refiner in aluminum alloy castings, though the mechanism by which it works is a subject of great debate.

The primary task of the present project was the development of aluminum cored welding wires which could be used to deliver grain-refining intermetallic additions to the aluminum weld pool. The major achievement has been the successful transfer of intermetallic inoculant particles across the arc and successful grain refinement of aluminum alloy weld metal. This transfer was achieved with particle filled cored aluminum welding wire developed with the CSM strip-to-core wire drawing machine..

2.2.1 Summary of Results: Advanced Aluminum Welding Consumable Development

A survey of the literature on nucleation, correlations, and theoretical calculations has been used to select promising addition elements from the transition metals, rare earth metals and alkaline earth metals. Alloying theory and solidification behavior was considered in this selection. Nucleating additions were required which are effective at small concentrations and provide stable high melting point intermetallic particles that can survive multiple welding passes.

Although cored welding wire has been used extensively in the steel industry, it has yet to be used in the aluminum industry. It was the goal of this research to develop a method of producing aluminum cored welding wire. Through the introduction of nucleation agents to the core of aluminum cored welding wire, the solidification of the weld metal can be controlled, and thus enhance grain refinement.

A manufacturing process for the production of cored aluminum welding wire, which will allow the addition of nucleation agents directly to aluminum alloy welds, has been developed. Cored consumables contain metal additions that are protected and contained within a protective sheath of metal until needed in the weld pool. The aluminum cored welding wire was produced on a rebuilt Russian wire machine. A 12.7 mm wide by 0.508 mm thick aluminum alloy 5052 strip was used in the forming operation as shown in Figure 4. This particular alloy was selected for its lack of titanium addition. In aluminum alloy welds, the alloy 5052 is commonly used as a welding electrode. The aluminum strip was spooled on a pancake and mounted at one end of the wire machine. It passed through eleven forming stages (u-shaped channel), a closing mechanism, and then wrapped around a capstand. The development required an aluminum strip with mechanical properties to be formable as to "strip to channel" step and then have sufficient strength to allow for wire drawing. This selection of material and the forming practice was achieved. A cross section of a typical metal filled core wire is shown in Figure 5.

Powder-filled cored aluminum welding consumables were produced with nucleating agent levels in the range of 0.01 to 1 weight percent. Powder-filled cored consumables allowed use of nucleating intermetallic phases in both peritectic and eutectic systems. Peritectic systems may be capable of forming intermetallic phases during solidification at small alloy element concentrations; however, nucleation problems may prevent the formation of sufficient nuclei during welding. Eutectic systems would require nucleating element concentrations above the eutectic composition to form the appropriate intermetallic phases rather than the primary aluminum phase. Powder-filled cored consumables offer the ability to add these phases directly in the form of master alloys.

Metal-filled weld aluminum wires has been produced on the CSM wire drawing system. It will require further development by a consumable manufacturer to increase the production rate due to forming and drawing difficulties that aluminum strip-to-metal filled cored wire forming exhibit.

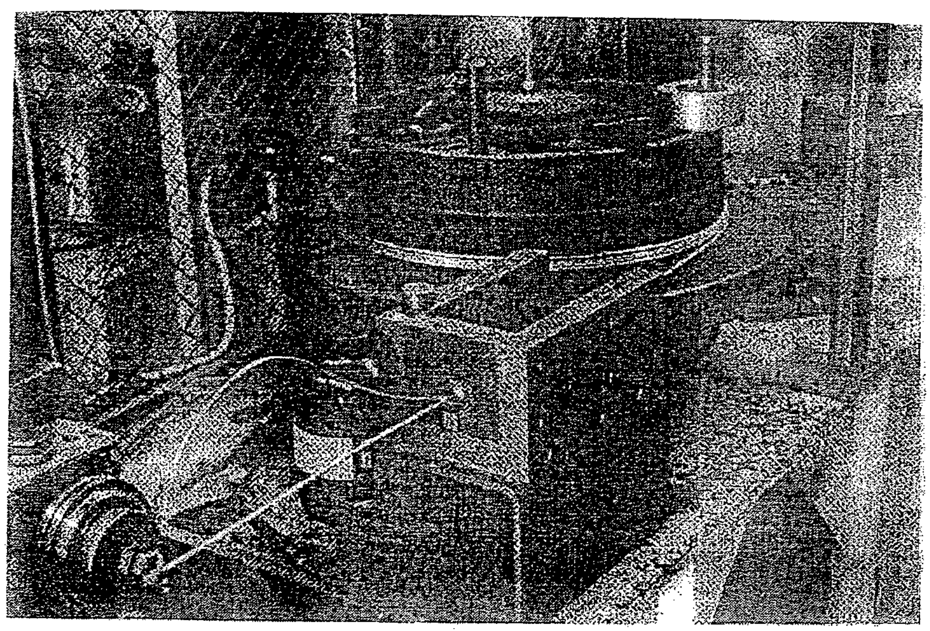

Figure 4. Photograph showing the wire drawing box, capstand, and the last stage in the wire forming process.

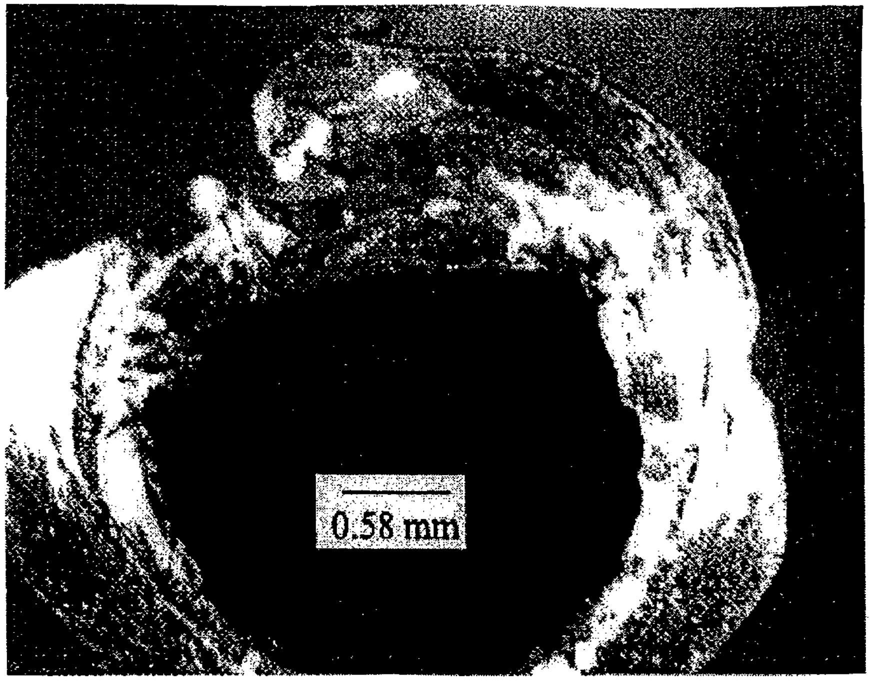

Figure 5. Photograph showing the cross-section of cored aluminum welding wire. The wire has a diameter of 0.170 inches (4.3 mm)

2.3 Weldable Magnesium Alloy for Transportation System

Magnesium alloys have recently received international attention as a material to further reduce weight in transportation systems (29, 30). If new magnesium alloys advance, numerous U.S. Army systems could take advantage of them for increased mobility and system performance. To stay current in these trends in light metal alloys, two reviews were prepared. Two papers described alloy theory concepts to achieve an advanced magnesium alloy that should offer significant improvements in formability, weldability, corrosion resistance and combustion resistance (31, 32). A third paper was prepared which reviews the weldability issues associated with magnesium alloys (33).

2.4 Specialty Welding Wires by the Strip to Cored Wire Process

The U.S. Army utilizes and depends on a large spectrum of alloys to achieve its mission. Some of these alloys are specialty alloys with very low user volumes requiring welding consumable manufacturers to address a limited market. These low volume consumables require costly small steel and aluminum heats at the primary mills and a labor intensive special material handling. With major reduction in the number of consumable manufacturers, the long term availability of manufacturers willing to produce these specialty consumables, especially at reasonable cost, is in question.

The metal-filled core wires offer a very versatile method of manufacturing economically and rapidly low volume specialty welding consumables. The ARO sponsored consumable research at CSM has developed an experimental mill to produce metal power-filled core wires for specialty alloy welding consumables for evaluations.

The metal powder filling of channeled strip and forming of cored wires to be used as gas metal arc welding consumables can achieve weld deposits of a large range of alloy compositions, microstructures and properties. To achieve the ability to produce wires with the proper additions (types, concentration, particle size) will require a full characterization of elemental transferability across the welding arc, and the behavior of the particulate additions with various welding parameters. The resulting correlations will be mechanistically modeled to allow accurate selection and filling of these cored wire consumables and to achieve acceptable weld grain refinement.

2.5 Electronic and Magnetic Property Measurement Techniques to Determine Weld Microstructure and Phase Stability and Alloy Aging

The electronic state of an alloy is one of the primary influences on phase stability. Engel and Brewer (34) and Hume-Rothery (35) have shown through correlations that elemental crystal structures, primary solubility and intermetallic phases can be predicted based electronic configuration and concentrations. Cho (36) has correlated many physical and mechanical properties to an electron to atom ratio, where the electron count for each atom is all the electrons above the last filled inert gas shell of that atom. With such an electronic signature to elemental and alloy microstructure and properties, it should be possible to use electronic and magnetic property measurements to assess alloy stability (37-40). The achievement of making electronic and magnetic property measurements to correlate directly with alloy theory will promote new approaches in alloy developments and offer a method of assessment of the remaining service life of time dependent alloys.

2.5.1 Electronic Property Measurements

In many alloy systems the electron concentration has been shown to be an important parameter that influences such factors as the extent of solid solubility, the presence of a crystallographic structure, the range and stability of intermediate phases, the formation of long-period superlattices, trends in lattice spacing, the number of vacant sites, the magnetic susceptibility, etc. (41). Hall and Seebeck coefficients and

electrical conductivity are properties to be used in this investigation for alloy stability assessment.

2.5.1.1 Hall Effect

When a conductor is placed in a magnetic field perpendicular to the direction of current flow, the Hall electric field is developed across the specimen in the direction perpendicular to both the current and the magnetic field, and proportional to the current density and magnetic field strength. The coefficient of proportionality, R_H, is called the Hall coefficient, and, in general could be divided into its two component parts, corresponding to the ordinary Hall effect present in all metals and the anomalous Hall effect present only in ferromagnetic metals. The ordinary Hall coefficient provides an opportunity to estimate the free carrier concentration:

$$R_H = \pm A_R \frac{1}{N_e} \qquad \textbf{(1)}$$

where N is the free carrier concentration, e is the electron charge magnitude, sign "-" corresponds to n-type conductivity (Fermi level, E_F, is located in the lower part of the energy band), and "+" corresponds to p-type conductivity with holes being dominant charge carriers (E_F in the upper part of the band). The so called Hall factor, A_R, in metals is close to 1 if the Fermi surface in the momentum space is of a simple shape. Its shape becomes very complicated and the Hall factor can significantly deviate from 1 for the intermediate E_F values corresponding to the transition from n- to p-type conductivity.

As the Hall measurements are primarily influenced by the electron concentration of the metallic matrix, the Hall coefficient should characterize the state of the metal matrix. Hall coefficient measurements have been performed on Palladium-Iron alloys (42). The dependence on temperature and concentration were investigated for alloys ranging from 0.5 to 99.5 at. pct. iron in the range of 2-300 K. The alloys provided a continuous series of disordered solid solutions. Alloys with less than 77 at. pct. iron have a face-centered cubic structure, and those phases with iron above 93 at. pct. have body-centered cubic structure. The changes in the crystal structure were found to alter the temperature dependence and the sign of the Hall coefficient.

Kittel (43) also illustrated electronically a phase change in the Cu-Sn alloy system as the tin addition raises the Fermi energy level into the corners of the Brillion zone resulting in an increase in the Hall constant from a negative value to a positive value seen at 25 at. pct. tin. The Hall effect and electrical resistance throughout the entire Iron-Cobalt alloy system has been investigated in a temperature range from

liquid nitrogen to 800 K (44). The composition dependence of Hall effect and resistivity determined that these minimum values were apparently due to the formation of a superstructure known to form in that compositional range. Hall effect measurements are dependent on the geometry of the specimen and with a large electrical carrier content will only generate very small measurable potentials. Thus, for metallic specimens, Hall measurements can only be achieved with thin films or with the use of very high magnetic fields.

2.5.1.2 Seebeck Effect (Thermopower)

A temperature gradient applied to a conductor results in diffusion of free carriers from the hot end of the sample to the cold one. If the electrical circuit is disconnected, the ends of the sample accumulate electrical charges of the opposite sign. Thus the Seebeck electric field appears, which causes the carrier drift in the opposite direction leading to the zero net current. The so-called phonon-drag effect can also contribute considerably to the measured Seebeck voltage, especially in metals. The phonon flux occurring under a temperature gradient imparts an additional momentum to the carriers moving down the temperature gradient and hence modifies thermal e.m.f.

The Seebeck voltage, V_S, is measured between two metallic electrodes with known thermoelectric properties (reference material). The Seebeck coefficient, S, of a material under investigation is determined from measurements using (42):

$$S = \frac{V_s}{\Delta T} - S_R \qquad (2)$$

where S_R is the Seebeck coefficient of the reference material, and ΔT is the temperature difference between reference electrodes which should be small enough to neglect the temperature dependence of S and S_R. Copper or Constantan are often used as reference material.

Like the Hall coefficient, S changes its sign and magnitude as E_F moves up from the bottom to the top of the energy band. Thus changes in carrier concentration due to alloying can be monitored by Seebeck measurements. From S dependencies on carrier concentration and temperature one can also derive information on density of states function, dominant scattering mechanism, presence and properties of the resonant (virtual) states on the background of the band spectrum, etc. Some specific features appear in these dependencies in alloys of transition metals due to the presence of a narrow high density-of-states bands on the background of wide bands. Changes in the phonon-drag peak in S(T) can indicate changes in electron-

phonon interaction. Seebeck coefficient magnitude and temperature dependence can be significantly affected by the phase transitions. Numerous examples of S changes with composition of alloys and phase transitions can be found, e.g. in (45) and (46).

Measurements of Seebeck effect as a method for monitoring changes in electronic properties of an alloy have some advantages as compared to the Hall effect measurements. Hall voltage is inversely proportional to the carder concentration and is very small for typical metals. In the polycrystalline samples with enhanced resistivity, the signal usually drowns in noise. There are no problems in measuring the Seebeck coefficient of a polycrystalline metal, or even of a powder. These measurements can be made on a sample of arbitrary shape and size.

2.5.2 Magnetic Property Measurements

Nondestructive determination of the microstructural constituents of materials have been conducted on several alloy systems. The correlation between magnetic susceptibility and the precipitation of solute in heat-treatable aluminum alloys has been investigated (47). The Aluminum-Copper, Aluminum-Zinc, and Aluminum-Magnesium alloy systems were studied. For both the Aluminum-Copper and Aluminum-Magnesium alloy systems, varying solute compositions were measured in two extreme tempers, completely annealed and as-quenched. Measurements on the Aluminum-Zinc alloy were carried out at temperatures high enough to assure a complete solid solution. The measured magnetic susceptibilities were compared to calculated magnetic susceptibilities based on a mixture of components not alloyed, but simply mixed together in their pure states without producing a new phase. The data indicate that the difference between the magnetic susceptibility of a mixture of pure components and an alloy of the same bulk composition is equivalent to the Pauli paramagnetism of the aluminum metal associated with the alloy phases. The study calculated the number of aluminum atoms affected by solute such that their Pauli paramagnetism was not measured. The calculations supported the existence of short-range order in dilute solid solutions. Calculation for the fully aged samples showed excellent agreement with predicted equilibrium phases. For example, in the aluminum-copper alloy, roughly two aluminum atoms were associated with each copper atom that corresponds to the predicted $CuAl_2$ phase.

The magnetic properties of metals are the result of the metallic electrons that belong to the crystal as a whole, and the localized electrons on each particular ion. For a metallic specimen like an Al - 4 wt. pct. Cu alloy, the measured bulk magnetic susceptibility will be the sum of three separate contributions; orbital

diamagnetism from the ion, diamagnetism and Pauli paramagnetism from the conducting electrons (48).

For most metals including aluminum, the Pauli paramagnetism is larger than both diamagnetic effects and the magnetic susceptibility is positive. The magnetism is based on the paramagnetism of the electrons that are free to move throughout space occupied by the metal. Because these electrons also provide a bonding mechanism, a correlation between magnetism and bonding or phase stability should exist.

Not all metals are paramagnetic. Although the density of states at the Fermi level is normal, which makes paramagnetic behavior of its valence electron quite normal, copper is diamagnetic. Copper comes at the end of the first long transition period, and it has a newly filled 3d shell. Because the radius of the d shell is large, the diamagnetic effect of each of these 3d electrons is large. The 3d state contains 10 electrons, and so the total diamagnetic behavior is large. These two factors - large orbit of 3d electrons and large number of 3d electrons - make the diamagnetism of the closed shells of Copper larger than the paramagnetism of the free 4s electron. Copper is thus weakly diamagnetic (49). Lindahl et al. (48) were able to follow the GP1, GP2, θ' and θ formation in A1 - 4 wt. pct. Cu alloys using magnetic susceptibility measurements.

Magnetic phase analysis has been used for the Iron-Carbon and Iron-Silicon systems (50, 51). These alloy systems have ferromagnetic phases with established magnetic characteristics. The spontaneous magnetizations were measured for the annealed samples at several temperatures. The overall sample magnetization is known to be the sum of the magnetization for individual phases times the respective fractions of these phases in the alloy. Then it is possible to solve for the fraction each phase occupies in the sample. For the Iron-Carbon system, these investigations were able to determine what composition of the alloy was precipitated as cementite (Fe3C) and what fraction contained carbon in solid solution as ferrite. Analysis of the Iron-Silicon system was able to map the phases present across the phase diagram at various temperatures. The study was able to chart the change in weight fraction of α, α'', and η phases during annealing.

2.5.3 Summary of Results: Use of Electronic Property Measurements for Alloy Microstructure and Phase Stability Determination

2.5.3.1 Prediction of Topologically Close-Packed Phase

Nickel based superalloys were developed in the early 1960s to withstand the high temperatures and corrosive environments in gas turbines and chemical plants. The occurrence of topologically close-packed (TCP) phases in these alloys adversely affects the mechanical and corrosion properties (52-55). The factors that control the formation of the TCP phases are the atom size, the electron vacancy, and the relative electronegativities of the atoms. Recent developments in alloying theory have led researchers to devise new methods to determine the susceptibility for the formation of a TCP phase in nickel and cobalt base superalloys. TCP phases can be divided into two general categories, Laves-type and Sigma-type phases (34, 35, 56-61).

PHACOMP is an electron based calculation technique that predicts the tendency of an austenitic alloy to precipitate TCP phases (37-39, 62, 63). The basis of this prediction is the atomic electron vacancy theory. Morinaga, Yukawa, Adachi and Ezaki (64, 65) have developed New PHACOMP in an attempt to predict the solid solubility of alloys. New PHACOMP is based on a Md parameter, which is an average energy level of the d-orbitals of alloying elements. Verification of New PHACOMP was accomplished by predicting the gamma/gamma plus sigma phase boundary of existing ternary phase diagrams (66). The prediction of sigma phase occurrence for nickel-based superalloys was carried out (67, 68). Cieslak and Olson (69-72) have investigated the use of New PHACOMP in many nickel base weldments.

2.5.3.2 Development of PHACOMP Non-Destructive Meter

Because there is both theoretical and experimental evidence that specific electronic and magnetic properties can be correlated to phase instability and microstructure, there is great promise in the development of an electronic or magnetic measuring technique or a combination of techniques to measure phase stability. The Hall and Seebeck coefficients provide information about the Fermi level, electron concentration and the density of state function for an alloy. The magnetic measurements of high transition metal alloys will allow for better understanding of the role of the d-orbital or f-orbital to bonding and phase stability. The electrical conductivity measurements, which are influenced by all the crystalline defects, give some information about level of defect structure in an alloy. Using a combination of these measurements, an analytical technique which plots data in electronic and magnetic property space, will be developed to determine the region (see figure 6) of alloy stability. A three parameter space diagram

will be used to identify the stability region. This stability region will be measured and not calculated from electronic models. This electro-magnetic space could be used as a map to locate the amount of sigma phase within a part and determine its remaining lifetime. These efforts are in progress with the new ARO granted (DURIP) electronic property equipment to develop the analytical practice for determining weld microstructure, phase stability and properties.

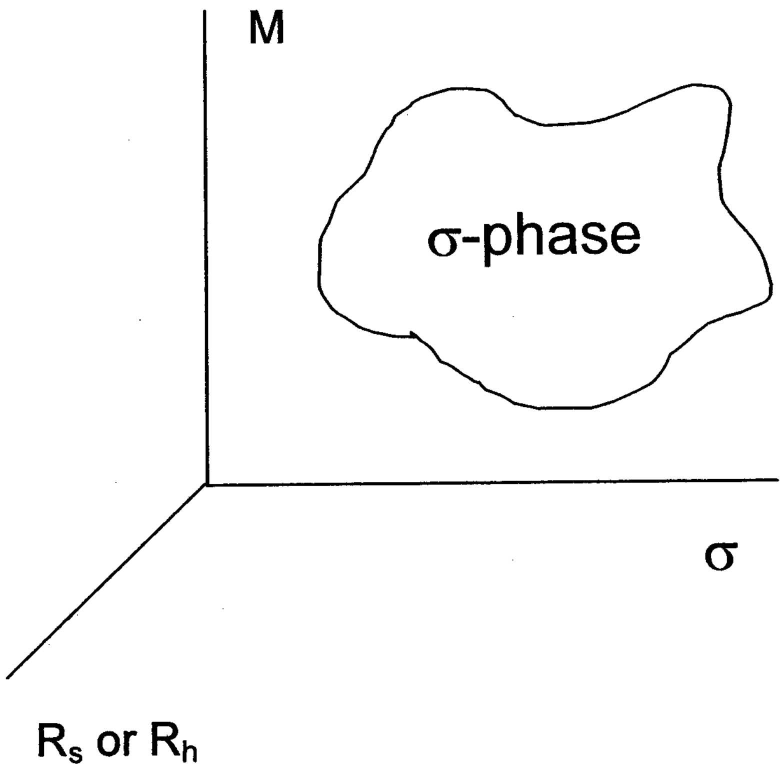

Figure 6. Simulated map of sigma phase susceptible region in electro-magnetic space, using the conductivity, Seebeck or Hall coefficient and magnetic measurements.

2.5.3.2 Electronic and Magnetic Measuring Techniques for Diffusible Hydrogen Content in Structural Alloys

Using the electronic alloy concepts being developed here for assessing weld microstructure phase stability and aging, electronic and magnetic property measurements were applied to nondestructively determine the diffusible hydrogen content on the actual structural welds rather as test coupons. In figure 7, the diffusible hydrogen content in Invar was correlated to Seebeck coefficient measurements.

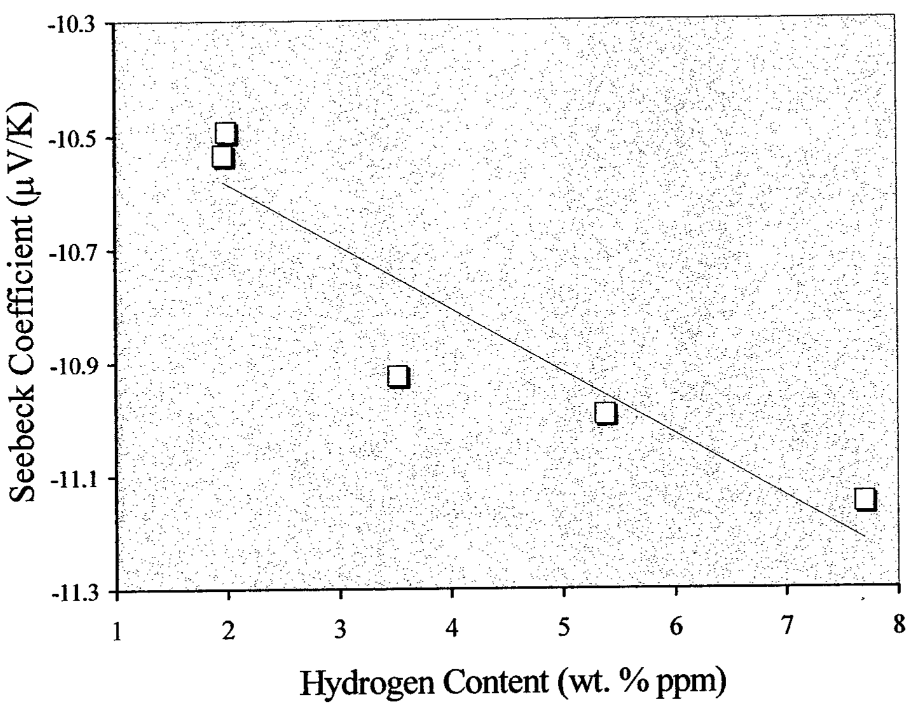

Figure 7. Correlation of Seebeck Coefficient with hydrogen content of Invar alloy.

3.0 List of Accomplishments During Present ARO Contract

1. Exothermic additions to Flux Cored Arc (FCA) wire can effectively increase heat input, weld bead cross-sectional area, penetration and deposition rate. The flux can also be modified to achieve self-shielding. The optimum welding process parameter space was determined.

2. The ability to make experimental aluminum consumables through metal powder additions to the core of a continuous aluminum sheath was achieved. Experimental wires with grain refining additions were prepared.

3. A fundamental grain refining investigation into the influences of specific intermetallic additions to the aluminum weld pool was performed. Alloy theory, nucleation and solidification concepts are being used to select inoculants and weld parameters to achieve stable grain refinement in multiple pass welds.

4. To assess new light metal alloys for transportation system, a literature review of the weldability of magnesium alloys and theoretical evaluations for more weldable and less combustible magnesium alloys were performed and published.

5. A DURIP grant equipped facility for measuring electronic properties of alloy welds to assess microstructure, phase stability and aging has been set up and investigations are in progress.

To date Seebeck coefficient measurements are being used to identify specific high alloys and efforts are in progress to produce a PHACOMP meter to assist in identifying alloys susceptible to sigma phase formation during high temperature service. The Seebeck coefficient has also been correlated to the diffusible hydrogen content of specific alloys. Efforts are in progress to assess the hydrogen content of a cathodically protected Nickel-Aluminum Bronze marine fastener used in submarine service. These fasteners get hydrogen-charged during cathodic protection and at high diffusible hydrogen contents, these fasteners are susceptible to cracking. If successful in measuring the hydrogen content with a contact electronic property measuring tool, a non-destructive test will be available to indicate fasteners to be removed from service.

4.0 Publications, Theses, Patents, and Awards during Present ARO Contract

4.1 Publications

List of publications from the ongoing ARO welding pyrochemical and metallurgical (core program) research at CSM:

1. J.H. Kim, R.H. Frost, and D.L. Olson, "Electrochemical Oxygen Transfer During Direct Current Arc Welding", Welding J., 77, pp. 488s-494s (1998).
2. D.L. Olson, S. Liu, and S. Caldwell, "Use of Intermetallic Alloys as Additions to Tungsten Electrodes", Proc. 3rd Pacific Rim Conf. On Adv. Mat. And Proc., (PRICM), pp.2265-2274, Honolulu, HAWAII, July 1998, TMS, Warrendale, PA (1998).
3. S.D. Kiser, C.W. Case, J.H. Devletian, J.F. King, J.C. Lippold, D.L. Olson, and C.L. Schmidt, Clad and Dissimilar Metals, AWS Handbook, 8th Edition, vol. 4, Chapter 6, pp. 333-389, American Welding Society, Miami, FL (1998).
4. J.W. Allen, D.L. Olson, and R.H. Frost, "Exothermically Assisted Shielded Metal Arc Welding", Welding Journal, 77 (7), pp. 277s-285s (1998).
5. D.L. Olson, V.I. Kaydanov, and D.W. Wenman, "Electronic and Magnetic Techniques to Determine Microstincture and Phase Stability", in Non Destructive Characterization of Materials IX, Amer. Inst. of Physics, AIP Conf. Proceedings 497, pp. 120-127, Melville, NY (1999).
6. D. Wenman, D.L. Olson, D.K. Matlock, and M.J. Cieslak, "Sigma Phase Formation Kinetics in Stainless Steel Laminate Composites", Trends in Welding Research, pp. 125-130, Pine Mtn., GA, ASM, Materials Park, OH (1999).
7. S. Liu and D.L. Olson, "Stepwise Methodology of Welding Flux Formulation from Rutile to CaO-CaF2 Grade", Intn. Conf. on Fluxes, Slags and Molten Salts, Sweden and Helsinki, Finland, June 12-18, 2000, Proc. on CD, Royal Institute of Technology, Sweden (2000).
8. D.L. Olson, "La Influencia De Los Gradientes Micostructurales en LAS Propiedades Y Comportamiento De LAS Soldaduras" (supporting literature: D.L. Olson, G.R. Edwards, S.Liu, and D.K. Matlock, "Non-Equilibrium Behavior of Weld Metal in Flux-Related Processes", Welding in the World, vol. 31 (2), pp. 142-154 (1993)), pp. 429-443, Proceedings II Conferencia y Exposicion del Caribe, Marzo 15-16, 2000, Caracas, Venezuela (2000).
9. D.L. Olson, B. Mishra, and D.W. Wenman, "Welding, Brazing, and Joining of Refractory Metals and Alloys", Reactive and Refractory Metals, Gordon and Breach, NY, NY, pp. XX (2000), Min. Proc. Ext. Met. Rev., vol. 22, pp. 1-23 (1999).
10. D.L. Olson, "Consumibles Para Electrodos Auto Protegidos (SMAW-FCAW), Asistidos Exothermicamente Para Soldaduras de Reparacion", pp. 182-190, Proceedings II Conferencia y Exposicion del Caribe, Marzo 15-16, 2000, Caracas,Venezuela (2000).
11. C.E. Cross, S. Liu, G.R. Edwards, and D.L. Olson, "Aluminum Welding", Handbook of Aluminum Metallurgy, Processes, and Equipment, Marcel Dekker, NY, to be published (2002).

12. D.L. Olson, D.W. Wenman, V.I. Kaydanov, C. Suryanarayana, and D. Eliezer, "The Search for Room Temperature Cubic Magnesium Alloys", Proc. of Magnesium 2000, 2nd Israeli Conference, pp. 165-172, 22-24 February 2000, Dead Sea, Israel, Magnesium Research Institute, Potash Home, Beer-Sheva, Israel (2000).
13. D.L. Olson, M. Marya, D.W. Wenman, J.D. Olivas, and D. Eliezer, "The Use of Alloy Theory to Enhance the Properties of Magnesium", Proc. of THERMEC 2000, pp., Las Vegas, NV, Dec. (2000).
14. M. Marya, D.L. Olson, and G.R. Edward, "Welding of Magnesium Alloys for Transportation Applications", Joining of Advanced and Specialty Materials III, pp 122-128, October 9-11, 2000, ASM Materials Week, St. Louis, MO, ASM, Materials Park, OH (2001).

4.2 Theses

1. Kenneth E. Johns III (1999), MS, "Grain Refining Enhancement in Aluminum Welds through the Introduction of Nucleation Agents to Aluminum Cored Welding Wire"
2. Stephen Henry Malene (2000), PhD, "Response of Exothermic Additions to the Flux-Cored Arc Welding Consumable Electrode"
3. Uriah David Otting (2000), ME, "Identification of Sigma Phase in Superalloys by Correlation with Electronic and Magnetic Properties"

4.3 Patents

No Patents

4.4 Awards

1. 1998 Light Metals Reactive Metal Award, TMS, San Diego (March 1999)
2. 1999 TTCP Achievement Award U.S. Department of Defense, Pentagon, Washington, D.C., (May 19, 2000)
3. Foreign Member of National Awarding of Science (Materials Science) of Ukraine, Kiev (April 2000)
4. Arata Medal, International Institute of Welding, Ljubljana, Slovenca (July 2001)

4.5 Scientific Personal

Professor David L. Olson Principle Investigator

Stephen H. Malene PhD student (graduated)

Kenneth E. John III, MS Student (graduated)

Douglas Wenman, PhD student (left program for personal reasons)

David Otting Uriah, ME (graduated)

Zachrey Smith, Undergraduate Laboratory Assistant

Dr. Daniela Zander, Post Doctoral Scientist

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